THE STRUCTURE OF METHYL ALPHA-HALOACRYLATE POLYMERS

BY

CHARLES WILLIAM FAIRBANKS

B.S., University of Wichita, 1940
M.S., University of Wichita, 1948

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
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R. UNIV. BIBLIOTHEEK LEIDEN

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Introduction

Treatment of 1,2-dihalo organic compounds with potassium iodide eliminates iodine (1), and the amount of iodine liberated is a measure of the number of 1,2-dihalo groups present in the compound. Using this reaction, Marvel and Cowan (2), have shown that 92 per cent of the halogen may be eliminated from the polymer of methyl α-bromoacrylate at 100°. This was considered sufficient evidence to conclude that the structure of this polymer was of the "head to head, tail to tail" configuration.

This is the only polymer which has been shown to have this configuration. Since it is an exception, Price (3), has pointed out that all the halogen might be elimated if there were only a very small number of "head to head, tail to tail"units in the polymer. This could take place through the loss of iodine from the small number of "head to head, tail to tail" units, the resulting unsaturation activating the remaining halogens so they could be eliminated as hydrogen bromide upon heating.

The present work was undertaken to determine, beyond a doubt, the correct structure of the methyl α-haloacrylate polymers.

Discussion of Results

The polymer of methyl α-bromoacrylate was treated with potassium iodine at room temperature to reduce the possibility of the loss of hydrogen bromide from the polymer. The amount of halogen eliminated from the polymer was determined in two ways:

(A) The iodine liberated was titrated with sodium thiosulfate and the amount of halogen eliminated from the polymer was calculated from these results. The best end points in this

titration were obtained using a potentiometric titration set-up. After treatment for one hundred and thirty-three days, about seventy per cent of the halogen had been eliminated.

(B) The product obtained from such treatment was analyzed for bromine and iodine. Such analysis showed that 87.3 per cent of the halogen had been removed from the polymer after allowing to stand for two hundred and one days.

Since there is little probility that any of the halogen would be lost as hydrogen bromide under these conditions, these results show that at least the majority of the polymer is of the "head to head, tail to tail" configuration.

The polymer of methly α-bromoacrylate was treated with potassium iodide at 100°. Analysis of the product showed that all the halogen had been removed. Similar experiments were run with nitrogen passing through the reaction mixture and standard base. There was no evidence of any appreciable loss of hydrohalogen acid under these conditions.

The polymer of methyl α-bromoacrylate was hydrolized with moist silver oxide; this product oxidized with lead tetraacetate and the resulting solution treated with 2,4-dinitrophenylhydrazine. The di-2,4-dinitrophenylhydrazone of α,α'-diketoadipic acid was the only product which could be isolated from the reaction mixture. This is the product to be expected if the bromo polymer were "head to head, tail to tail".

Treatment of a solution of methyl α-bromoacrylate polymer with zinc, at high dilution, removed all the bromine with no cross-linking. Flory (4), has calculated statistically that only 86.47 per cent of the halogen could possibly be removed from a "head to tail" type structure, while only 81.60 per cent of the halogen could be removed from a completely random polymer. This indicates that the polymer is completely "head to head, tail to tail".

Ultraviolet spectra were obtained for the products obtained from the treatment of methyl α-bromoacrylate polymer with zinc, at high dilution, potassium iodide and heat, dimethyl

fumarate, and dimethyl maleate. The curves for the dimethyl fumarate and the products of the bromo polymer were nearly identical, each peak occurring at exactly the same wave length. The curve for dimethyl maleate was similar, but several peaks present in the spectra of the dehalogenated polymer were missing. This proves conclusively that these four products all have the same type of structure. The only way the polymer could have this structure would be if the polymer of methyl α-bromoacrylate were completely "head to head, tail to tail".

The structure of the polymer of methyl α-bromoacrylate has been shown to be completely "head to head, tail to tail".

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VITA

Charles William Fairbanks was born March 27, 1918, in Wichita, Kansas. After attending the public schools of Wichita and graduating from Wichita High School North in June of 1936, he entered the University of Wichita and received the degree of Bachelor of Science from that institution in June of 1940. Another year was spent in post-graduate work at that University. Following service in the Army of the United States from October, 1941, to January, 1946, he reentered the University of Wichita and received the degree of Master of Science in May, 1948. From January, 1946, to August, 1947, he was a Teaching Assistant at the University of Wichita. He entered the Graduate College of the University of Illinois in September, 1947. He held a Teaching Assistantship from September, 1948, to August, 1949, and a University of Illinois Fellowship from September, 1949, to June, 1950.

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